Suppression concentration of clean agents exposed to a continuously energized heated metal surface

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Abstract

An apparatus for the determination of autoignition temperature of hydrocarbon fuels has been used to measure the change in ignition temperature of a stoichiometric mixture of ethene/air with and without the addition of a suppressant: N_2, IG-542, HFC-23, HFC-227ea, FC-218 or FC-3-1-10. When exposed to a heated metal surface of nickel, a fuel/air stream with clean agent added generally required higher temperatures to ignite than when no agent was present. For some agents at low concentrations, it was found that ignition occurred at temperatures lower than when no agent was present. As agent concentration was increased, ignition became harder, i.e., the temperature required for ignition was higher. For each of these suppressants, with foil temperatures approaching 1000°C, the agent concentration necessary to prevent ignition of the ethene/air mixture exceeded the total flooding and met or exceeded the inerting design concentrations recommended in NFPA 2001, the Standard on Clean Agent Fire Extinguishing Systems. Published by Elsevier Science Ltd.

1. Introduction

The National Fire Protection Association *Standard on Clean Agent Fire Extinguishing Systems*, NFPA 2001 [1], was developed in response to international restrictions on the production and use of halon 1301 (CF_3Br). The standard addresses minimum

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requirements for total flooding clean agent fire extinguishing systems. The minimum effective concentration to suppress the fire is estimated, assuming the agent is totally gasified and uniformly distributed throughout the entire enclosure, based on 120% of the cup burner value. This safety factor on the cup burner value is meant to account for nonuniform distribution and leakage of agent from the enclosure. It does not address additional factors to determine effective agent concentration under conditions where energized electrical equipment cannot be disconnected from electrical sources – prior to, during, or after the release of a clean agent on a Class C fire.

NFPA 2001 provides no guidance regarding the concentration of agent required to suppress an energized ignition source (and its associated elevated temperatures). In the event that conditions for reflash exist, Section 3–4.2.1 of the Standard states that "the inerting concentration shall be used". While this paragraph is commonly interpreted as applying to Class B fires, a similarly hazardous condition could exist in a Class C fire, in which energized surfaces or elevated temperatures are in close proximity to flammable materials contained in electrical equipment. Section A-3-7 touches on the subject with general recommendations that, in the event of a continuously energized ignition source, "consideration should be given to the use of extended discharge, the use of higher initial concentration, and the possibility of the formation of combustion and decomposition by-products". How much longer the discharge or higher the concentration should be is not specified.

A series of fire suppression tests were conducted by Driscoll and Rivers [2] to ascertain the effect of an electrically energized wire on the concentration of agent needed to extinguish solid and liquid fuel flames. In one experiment, a bare electrical wire was placed above the liquid surface of a cup burner apparatus. Three different alternative agents, with CF_3Br as a baseline, were added to the air stream and the minimum extinguishment concentration was recorded for each at several different electrical power settings. A clear trend between increasing electrical power and the minimum extinguishment concentration showed that values significantly greater than the published cup burner concentration of agent were necessary to extinguish the energized cup burner flame. In a second experimental setup, nichrome wire was wrapped around or placed through blocks of polymethyl-methacrylate (PMMA) fuel specimens. A similar relationship between increasing power level and additional extinguishing concentration required was noted in these experiments. In general, higher electrical power was found to require more agent to extinguish the fire.

In an effort to quantify the effectiveness of various agents to suppress electrically energized ignition, Hamins and Borthwick [3] determined the impact of the fire suppressants on the possible ignition of reactants flowing over a hot metal surface. They measured the changes in ignition temperature of stoichiometric mixtures of methane/air, ethene/air and propane/air as a function of agent concentration for five selected agents. Their primary emphasis was on the reignition problem associated with the use of a fire suppressant in the vicinity of hot surfaces. The basic scenario involved the initial release of agent and the suppression of the fire. Because of the presence of fuel vapor, a flammable mixture may still exist that could lead to reignition by a hot surface. They found that conditions leading to reignition are controlled by

the time/temperature history of the reactive mixture and to a lesser extent by the type of metal surface and chemical composition of the fuel.

Expanding on the work of Hamins and Borthwick, the current study investigates the use of a short-duration auto-ignition apparatus [4] to quantify the effectiveness of six clean agents in preventing the ignition of a stoichiometric mixture of ethene/air, simulating a possible reflash condition. Use of a gaseous fuel represents a most dangerous case, e.g., when electrical insulation containing polyethylene is pyrolyzed. Ethene was used as the fuel because it is a major decomposition product of some polymer materials [5] and because Smyth and Bryner [4] found ethene/air mixtures to have the lowest auto-ignition temperature of the alkenes and alkanes tested.

2. Materials

The behavior of six clean agents was examined under conditions simulating the exposure of pyrolysis gases to an electrically energized metal surface. These six agents are listed in Table 1 along with relevant physical properties: chemical formula, molecular weight, vapor pressure at 25°C, specific heat, and normal boiling point. Two agents, N_2 and IG-541 (also known as INERGEN,[1] a mixture of 52% N_2, 40% Ar, and 8% CO_2), are physically acting agents; two are hydrofluorocarbons: HFC-23 and HFC-227ea; and two are perfluorocarbons: FC-218 and FC-3-1-10. All agents have previously been considered for Class A and B applications and are nonconducting, making them suitable for Class C applications. Bottles of compressed fuel, 99.5% pure ethene (C_2H_4), and dry air were used.

3. Experimental method

Tests were conducted using a short-duration auto-ignition temperature apparatus developed in a previous study [4] and described in the schematic diagram of Fig. 1. The apparatus consists of the following: a premixed-flame burner assembly; foil holder assembly with thermocouples; mass flow controllers for fuel, air, and agent; DC power supply; and a data acquisition system.

The premixed-flame burner assembly consists of a chamber to ensure complete mixing of fuel, air, and agent, and a porous burner head designed to prevent flashback upon ignition. A 22 mm long × 11 mm diameter quartz chimney is on top of the burner head to isolate the fuel–air–agent gas stream from ambient air until the flow is within 6.4 mm of the hot surface. The burner is positioned such that the initial fuel–air–agent contact point on the foil surface is near the lower of two thermocouples.

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[1] Certain trade names and company products are mentioned in this report in order to specify adequately the materials or equipment used. In no case does such an identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

Table 1
Properties of clean agents [1,10,11]

Suppressant	Nitrogen	IG-541	HFC-23	HFC-227ea	FC-218	FC-3-1-10
Chemical formula (% by vol)	N_2	52% N_2 40% Ar 8% CO_2	CHF_3	C_3HF_7	C_3F_8	C_4F_{10}
Molecular weight (g/mol)	28.0	34.0	70.0	170.0	188.0	238.0
Vapor pressure at 25°C (MPa)	Super Critical	Super Critical	4.74 [10] (Near Critical)	0.457	0.880	0.268
C_p, Specific heat at 25°C (J/g °C)	1.04	0.776[a]	0.736	0.820	0.798	0.80
Normal boiling point at 101 kPa (°C)	− 196	Indeterminate	− 82.0	− 16.4	− 36.8	− 2.06

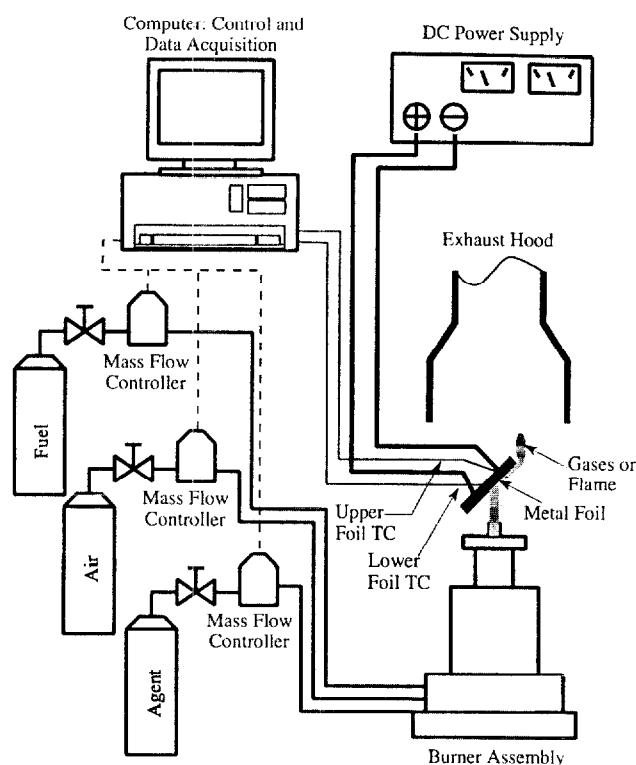[a]Calculated from the sum of the (C_p × mass fraction) for each component.

Fig. 1. Schematic drawing of apparatus used to determine ignition temperature of fuel–air–agent mixtures.

The foil holder assembly is spring loaded to compensate for metal expansion during heating and to maintain contact between the foil and electrical source and two thermocouples. The metal foil used in these experiments was nickel, 0.013 mm thick, and cut to an overall size of 24 mm × 102 mm. The foil is cut, notched, and folded as described in Ref. [4] to ensure that the maximum temperature occurrs in the center region of the foil surface. While under power, the foil glows red hot in a vertical stripe between the notches and two small round shadows can be seen, representing the thermocouples' contact points. The shiny side of the foil is exposed to the fuel–air–agent mixture and the reverse side is in contact with the two thermocouples. The holder assembly is positioned over the burner assembly at a 45° approach angle of the fuel–air–agent mixture. This results in a contact (residence) time of approximately 100 ms.

The thermocouple probes are located 1.6 mm from the upper edge of the metal foil and 3.2 mm from the folded lower edge of the foil. The proximity of the gas jet contact point explains the consistently hotter temperature on the lower thermocouple. The chromel–alumel subminiature thermocouples are constructed of two 38-μm wires

electrically insulated by magnesium oxide within a 0.25-mm stainless-steel sheath. The upper thermocouple was approximately 60°C cooler than the lower thermocouple. Due to imperfect contact between the thermocouples and the foil, and heat losses caused by the thermocouple, the foil temperature seen by the gas mixture may have been higher. An optical pyrometer used in Ref. [4] found that the foil temperature was 50–60°C higher. The temperatures reported throughout are those measured at the lower thermocouple. It has previously been estimated [3] that uncertainity in the measurement process was ± 11°C at best, based on a propagation of error analysis.

The fuel, air, and agent flows are controlled by a set of calibrated mass flow controllers. The fuel and air mixture is maintained constant at stoichiometric conditions, a ratio of 1 : 14.3, for all concentrations of agent. The total volume flow of fuel, air, and agent is held constant such that the average flow velocity exiting the quartz tube was consistently 160 mm/s.

Electrical current to the nickel foil is provided by a pair of 20 V power supplies wired in parallel to provide a maximum flow of 40 A, capable of heating the foil up to 1000°C. Temperatures higher than this were found to cause the nickel foil to break. A computerized acquisition system collected data from the two thermocouples and controlled the mass flow controllers.

A new foil was used with each agent. After mounting of the metal foil, it was annealed at approximately 1000°C. With each new foil, experiments were conducted first without agent, using only ethene/air mixtures. Subsequent experiments were performed with increasing concentrations of fire suppressant. The measurement process with or without agent was repeated three to five times to check reproducibility. Smyth and Bryner [4] found ignition temperatures of pure ethene/air mixtures using nickel foil to vary ± 24°C.

4. Results

Experiments were performed to determine the hot metal surface ignition temperature in the presence and absence of clean fire suppressant agents. For a chosen agent mole fraction, the fuel–air–agent mixture flowed over the electrically heated metal foil and the foil temperature was increased until flames were visible or until the lower thermocouple on the foil reached 1000°C.

Because metal foil positioning and tensioning affected the measured foil temperature, baseline ethene/air mixture experiments were conducted prior to the addition of any agent. The data for each agent are presented as a temperature change relative to the ethene air mixture ignition temperature for that set of experiments and for different agent concentrations. Replicate tests showed measurement errors that were sometimes greater than the differences between adjacent values. However, a distinction could be made between active flaming and no ignition away from the foil surface. Each data point in the figures represents the average of three to five replicates. Data points labeled as no ignition are effectively single determinations. At high agent concentrations, a distinct ignition event was difficult to define. The presence of random flashes, flickering, and glowing in the gas phase near or attached to the heated nickel

foil were detectable by visual inspection and by spikes in the temperature detected at the foil surface. The transient occurrences were taken as ignition events. Such a definition for ignition is appropriate from a safety standpoint since in an actual situation, the opportunity for the flammable gas mixture to remain in contact with a hot surface could be considerably longer. And, further, it is the goal of a suppressant evaluation test to examine the limit of ignition. The determination of the actual risk imposed by such an event is beyond the scope of this investigation. Therefore, in the following discussion "no ignition" describes the absence of any indication of combustion.

The average foil thermocouple temperature for ignition of stoichiometric ethene/air mixtures for all tests was found to be 750 $\pm$ 34°C. This compares with that found by Smyth and Bryner [4], 803 $\pm$ 24°C, and Hamins and Brothwick [3], 760 $\pm$ 11°C. While measurement uncertainty was a function of agent and agent volume fraction, it was found to be the same order of magnitude as the uncertainty observed with the ethene/air mixture.

4.1. Inert gas agents

Two substances were tested that NFPA 2001 classifies as inert agents – N_2 and IG-541. Fig. 2 shows the effect of increasing concentration of these inert agents on the thermocouple foil temperature necessary to ignite a stoichiometric mixture of ethene
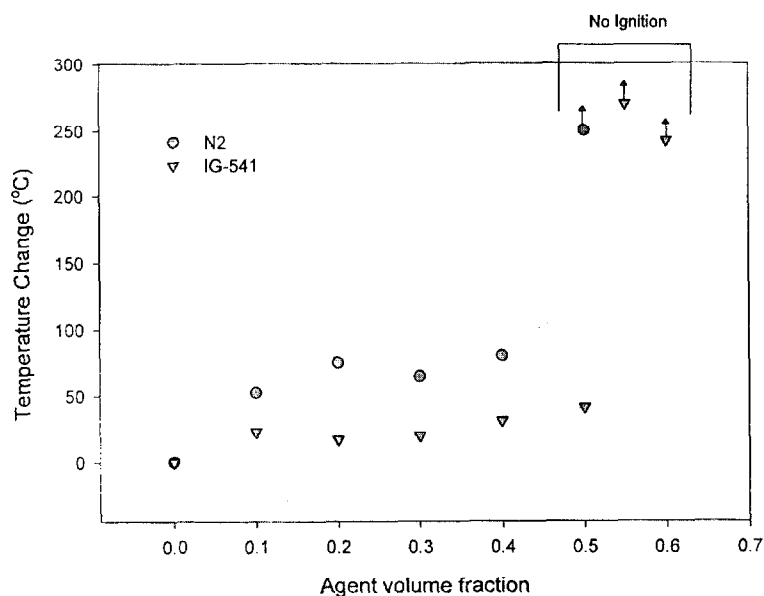

Fig. 2. N2 and IG-541 volume fraction impact on ignition temperature as detected by the lower thermocouple, normalized at the ignition thermocouple foil temperature of stoichiometric ethene/air. Uncertainty is $\pm$ 34 C.

and air. The increase in temperature for N_2 and IG-541 is approximately 70 and 30°C, respectively, above the baseline ignition temperature for agent volume fraction between 0.10 and 0.40. As the agent volume fraction was increased, the position of the ignition moved from the top of the burner tubes (at an agent volume fraction of 0.10) to the surface of the heated nickel foil (at 0.40). The change in flame location can be explained by the effect of the suppressants on the burning velocity of the mixture [6]. A small amount of suppressant did not sufficiently suppress the burning velocity, so the mixture flashed back to the quartz chimney where it was stabilized by the heat loss to the chimney. At the higher concentrations of agent, the burning velocity was reduced to the point that only in the close presence of the energized foil were the temperature conditions and residence times conducive to maintain combustion. At agent volume fractions of 0.50 for N_2 and 0.55 for IG-541, no visible flames were observed at the maximum foil temperature. This is indicated by an up-arrow attached to the symbol.

4.2. Halocarbon agents

Four halocarbon agents were evaluated: HFC-23, HFC-227ea, FC-218, and FC-3-1-10. Similar to the inert agents, as concentrations were increased, the position of the flame migrated from the chimney to the foil surface until a concentration was reached where no visible flame was observed. For some agents, a transition concentration existed where chemical reactions were observed as flashing, flickering, or glowing near or attached to the hot nickel foil. In a nonuniform mixture of agent and combustible gases, under different flow conditions these borderline reactions potentially could self-propagate, resulting in reignition.

Fig. 3 shows the effect of HFC-23 and HFC-227ea concentration on ignition. Increasing the amount of HFC-23 results in a rise in the foil thermocouple temperature necessary to cause ignition of the stoichiometric ethene/air mixture, from 12°C at an agent volume fraction of 0.05 to over 100°C at an HFC-23 volume fraction of 0.20. At a volume fraction of 0.25, no ignition was observed at a maximum foil thermocouple reading of 220°C above the baseline ignition temperature of an ethene–air mixture. This is indicated by an up-arrow attached to the symbol. Ignition may be possible at temperatures higher than those tested here. For HFC-227ea, at agent volume fractions of less than 0.08, the ignition temperature of the ethene–air mixture is actually slightly reduced. At these concentrations, the presence of the agent appears to enhance the ignition propensity of an ethene–air mixture. At agent volume fractions above 0.12, increasing the mole fraction of HFC-227ea results in an increase in the ignition temperature of the mixture. Above 0.15, no ignition was observed up to the maximum temperature tested here. At 0.25 agent volume fraction, light gray smoke was visible at the top of the heated nickel foil. Hamins and Borthwick [3] noted that, while concentrations of HFC-227ea above 0.10 would not support flaming ignition in a mixture of methane–air, black smoke was observed to roll off the hot metal surface.

Fig. 4 shows the effect of FC-218 and FC-3-1-10 levels on the foil thermocouple temperature at ignition. As with the other agents, the flame position shifted to the heated nickel surface as agent concentration was increased. For FC-218, the data
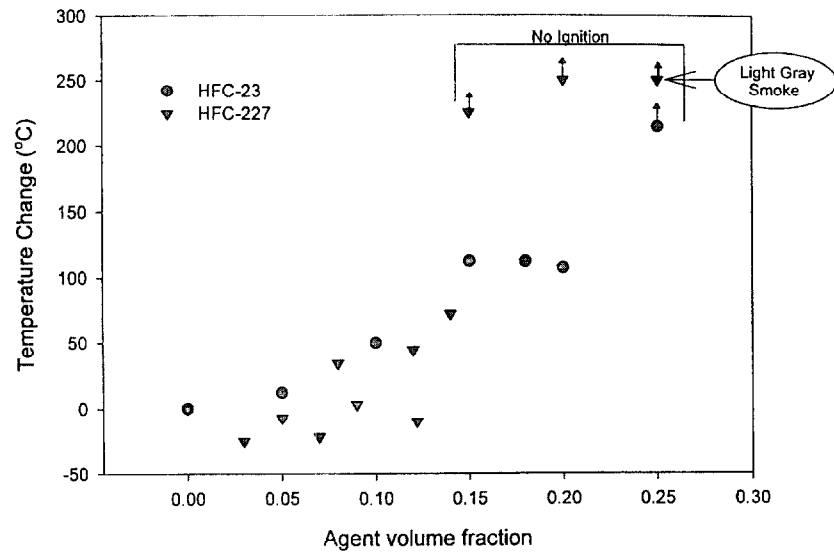
Fig. 3. HFC-23 and HFC-227ea volume fraction impact on ignition temperature as detected by the lower thermocouple, normalized at the ignition thermocouple foil temperature of stoichiometric ethene/air. Uncertainty is ± 34°C.
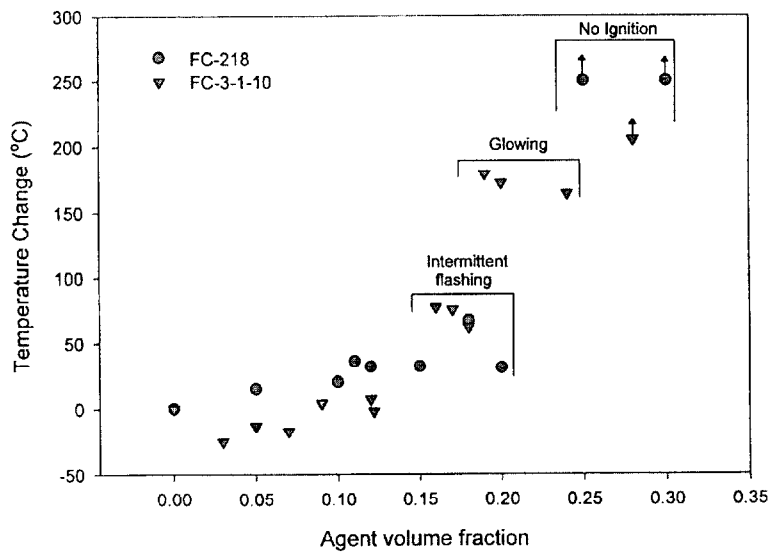

Fig. 4. FC-218 and FC-3-1-10 volume fraction impact on ignition temperature as detected by the lower thermocouple, normalized at the ignition thermocouple foil temperature of stoichiometric ethene/air. Uncertainty is ± 34°C.

show a small dependence of ignition temperature on agent volume fraction between 0.05 and 0.11. Between 0.11 and 0.20, no appreciable change in temperature was noted. At 0.18 and 0.20, ignition was observed at 50°C above the ethene/air ignition temperature as a series of random intermittent flashes – this is noted in the figure. At low volume fractions of FC-3-1-10, between 0.03 and about 0.09, the data show a weak enhancement in the ignition of ethene and air mixture, i.e., reduction in the nickel foil temperature that results in ignition of the mixture. Above about 0.12, FC-3-1-10 suppresses the ignition of ethene–air mixture, i.e., requires higher nickel foil surface temperatures. As the concentration is increased, the nature of the ignition process changes. Below 0.15 there is a distinct flaming ignition event. The location of the stable flame moves from the surface of the burner to the surface of the heated nickel foil. Over the range of 0.16–0.19 ignition becomes intermittent flashing. The temperature over this regime is approximately 70°C above the normal ignition temperature of an ethene–air mixture. Above 0.20, foil temperature increases of about 170°C are accompanied by a glow, which may indicate combustion. Under these conditions, the ignition event is very transient and difficult to define. At a volume fraction of about 0.28, no ignition was observed for FC-3-1-10 to the maximum temperature tested.

5. Discussion

Agent effectiveness is related inversely to the volume fraction necessary to suppress ignition on a heated metal surface. The greater the temperature required for ignition for a given volume fraction the more efficient the agent. Prior work [3] showed that in a stoichiometric ethene/air mixture the addition of CF_3Br, at a volume fraction of 0.010, increased the ignition temperature of the mixture by about 220°C. Only CF_3I, at a volume fraction of about 0.015, was found to be nearly as effective in suppressing ignition [3].

A 220°C increase corresponds to a nickel plate temperature of about 970°C. At this temperature, the volume fraction necessary to effectively prevent ignition ranges from 0.14 to 0.55 for the six clean agents tested in this study, as shown in Table 2. Total flooding design concentrations (n-heptane cup burner suppressant volume fractions [1,7,8] plus the additional 20%) and inerting concentrations (values listed are those for inerting propane [1] plus the safety factor of 10%) recommended by NFPA 2001 are also listed in the table. The range of values for a single agent corresponds to the range given in NFPA 2001 or the other references. At foil thermocouple temperatures approaching 1000°C, the hot surface suppression concentration exceeds all values recommended for total flooding (the cup burner plus 20%), by as much as four times. When compared to the recommended inerting value (for propane), the hot surface suppression concentration is double that recommended for FC-3-1-10, and matching for the other five agents.

Previous work by Driscoll and Rivers [2] stated that the presence of a hot wire in the cup burner, which represents a shorter residence time in comparison to the current work, required increased suppressant concentration by a factor of two. This

Table 2

Comparison of hot surface ignition results to published cup burner data [1,7,8] and inerting concentrations [1,12] with NFPA 2001 safety factors: +20% for total flooding, +10% for inerting design concentration

Agent	Test Fuel	Hot surface (940–1000°C) (Volume fraction) ethene/air	Cup burner value + 20% (Volume fraction) n-heptane/air	Inerting concentration + 10% (Volume fraction) propane/air
N₂		0.40–0.50	0.36–0.38	0.53
IG-541		0.50–0.55	0.35	0.54
HFC-23		0.20–0.25	0.14–0.15	0.22
HFC-227ea		0.14–0.15	0.070–0.079	0.13
FC-218		0.20–0.25	0.074–0.084	Not available
FC-3-1-10		0.24–0.28	0.060–0.071	0.11

is consistent with the work of Sano and Yamashita [9] on premixed methane air mixtures ignited by a heated plate. They found that the ignition delay initially decreased exponentially with increasing area of the hot surface. However, for a hot surface area greater than $20 \, mm^2$, the ignition delay approached a constant value.

6. Summary and conclusions

When exposed to a heated nickel surface for short periods of time, the surface thermocouple temperature required to ignite a stoichiometric mixture of ethene and air is $750 \pm 34°C$. In general, the addition of a clean agent to the fuel/air stream requires higher indicated surface temperatures than when no agent is present. However, in the case of HFC-227 and FC-3-1-10, the temperature required for ignition was slightly reduced when the agents were present in volume fractions below 0.08. The experimental data suggest a relationship between the number of fluorine atoms in the agent and the agent's ability to inhibit hot surface ignition.

The volume fraction of the agents tested necessary to prevent ignition of a stoichiometric mixture of ethene and air on a nickel surface approaching 1000°C can be several times the value found with the cup burner test apparatus. For the inert gases and HFCs, the ignition suppression concentrations are close to the inertion design criteria recommended in NFPA 2001 for propane/air mixtures. An exception is that the minimum concentration required for FC-3-1-10 is more than twice the NFPA 2001 value recommendation for inertion. Several explanations are possible. One is that FC-3-1-10 inhibition properties are more sensitive to the higher temperatures in this test, another is that there is increased catalytic activity on the surface between the agent and the nickel. No published data are available for the inertion concentration in propane of the other perfluorocarbon, FC-218, so it is not possible to compare this result to another fully fluorinated alkane.

An important conclusion to be drawn from these results is that in the presence of an electrically heated metal surface, a total flooding suppressant design concentration of 120% times the cup burner value may be insufficient to prevent reignition of a build up of flammable gases from adjacent pyrolyzing polymers.

Acknowledgements

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